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(19)

(54) IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF MAGNESIUM SILICATES

(71)   We, LAPORTE INDUSTRIES LIMITED, a British Company of Hanover House, 14 Hanover Square, London, W.1. do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5   This invention relates to a process for the synthesis of hydrous magnesium silicates.

The name "hectorite" has been ascribed to a natural trioctahedral smectite found at Hector, California, U.S.A. This clay is a hydrous magnesium silicate having the ideal composition $Si_8Mg_6O_{20}(OH)_4$ modified by having a portion of the Mg^{+2} and OH^- ions replaced by Li^+ and F^- ions. The synthesis of hydrous magnesium silicates similar to natural hectorite has 10 been described by Granquist and Pollack in "Clays and Clay Minerals" Volume 8 (Proceedings of the 8th National Conference on Clays and Clay Minerals) Pages 150-169. In the process described by Granquist gels of magnesium hydroxide and of silica are produced separately, are washed, are combined and are redispersed in water to form a suspension. Lithium hydroxide or lithium fluoride and sodium hydroxide are added to the suspension 15 which is then treated hydrothermally by refluxing it with stirring until a product having a crystal structure similar to that of hectorite is formed.

While Granquist's product has a crystal structure similar to natural hectorite it does not have good rheological properties. A standard yardstick of rheological properties of a substance is provided by measuring the Bingham Yield Value of an aqueous dispersion of the substance. 20 The term Bingham Yield Value (also known as Bingham Yield Stress, these terms being alternatives for the same property) is referred to in standard works on rheology for example in "Rheology Theory and Applications" F. R. Eirich (Acad. Press) Volume 1 (1956) Page 658 and "Colloidal Dispersions" L. K. Fischer (N.Y. Bureau of Standards) 2nd Edition 1953 Pages 150-170 and "The Chemistry and Physics of Clays and other Ceramic Materials" 25 3rd Edition Page 463, A. B. Searle and R. W. Grimshaw.

The Bingham Yield Value may be determined by first obtaining a flow curve relating the shear stress to the rate of shear and then extrapolating the straight line section of the curve to the shear stress axis the intercept being the Bingham Yield Value. It can conveniently be determined on any viscometer capable of measuring a range of shear rates and shear stresses. 30 The product of Granquist, when in the form of a dispersion obtained using 2g silicate and 100ml tap water, gives a Bingham Yield Value of only about 15 dynes per cm². This is a very low value, inferior to that given by natural hectorite. It also gives a low static gel strength.

Processes for the production of synthetic hydrous magnesium silicates having a crystal structure similar to natural hectorite but having better rheological properties than natural 35 hectorite have been described in British Patents 1,054,111 and 1,213,122. These processes describe the production of synthetic hydrous magnesium silicates having a characteristic hectorite-like structure and having varying contents of lithium and fluorine, by a process essentially involving direct coprecipitation of a magnesium silicate.

The process described in British Patent No. 1,054,111 involves forming a slurry by co- 40 precipitation by slowly combining with heating and agitation in an aqueous medium a constituent providing the magnesium ions with constituents providing the silicon (as silicate), hydroxyl and sodium ions and treating the precipitate hydrothermally. The concentration of the slurry is desirably such that the concentration of the product formed is from 1 % to 8 % by weight preferably 4 % by weight. The hydrous magnesium silicate contains fluorine and lithium. 45 The process described in British Patent No. 1,213,122 involves precipitating a magnesium

silicate by combining an aqueous solution of a water soluble magnesium salt with an aqueous alkaline solution of one or more sodium compounds in the presence of dissolved silicon compound and hydrothermally treating the precipitate under pressure. The concentration of the precipitate is preferably not more than 5% by weight. The hydrous magnesium silicate product contains no fluorine and optionally contains lithium.

The products of the processes of the two British Patents are also characterised by providing dispersions giving exceedingly high Bingham Yield Values in excess of any known to be given by natural hectorite dispersions and usually above 40, for example from about 50 to 250, dynes per cm² as a 2% dispersion in tap water, and high static gel strength. Such products have found widespread use by reason of their excellent rheological properties.

According to one aspect the present invention provides a process for the synthesis of a hydrous magnesium silicate having a crystal structure similar to that of hectorite and having the general formula

$$[Si_a \ (Mg_aLi_bH_c)O_{20}(OH)_{4-y}F_y]^{z-} \quad zM^+$$

wherein a, b, c, y, z and M have the values:—
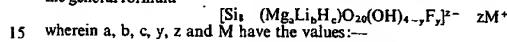
$$a \text{ is } 4.95 \text{ to } 5.7$$
$$b \text{ is from } 0 \text{ to } 1.05$$
$$c \text{ is from } 0 \text{ to } <2$$
$$a + b + c \text{ is from } >4 \text{ to } <8$$
$$y \text{ is from } 0 \text{ to } <4$$
$$z = 12-2a-b-c$$
$$M \text{ is } Na^+ \text{ or } Li^+$$

comprising the sequential steps of forming an aqueous suspension of magnesium carbonate, forming a silica precipitate in the aqueous suspension of magnesium carbonate, the proportions of magnesium provided by the magnesium carbonate and silica precipitated in the suspension corresponding to that of the formula of the magnesium silicate, maintaining the resulting mixture of magnesium carbonate and silica in the wet state and subjecting it to hydrothermal treatment by heating it in an aqueous medium·and in the presence of the remaining constituents of the magnesium silicate in proportions within the ranges specified in the general formula thereof and in the presence of excess dissolved sodium or lithium compound over that required to form the cation of the magnesium silicate until crystal growth occurs and separating the resulting crystalline product.

The present invention is to be distinguished from the processes described in British Patents No. 1,054,111 and 1,213,122 in that, in those processes, the magnesium compound and the silica are coprecipitated. Clearly the benefits of the present invention may be obtained at least partly by including only a part of the magnesium carbonate in the preformed suspension and therefore the invention is not strictly limited to the whole of the magnesium carbonate being in the preformed suspension. As the proportion of magnesium carbonate included by known means, for example coprecipitation, increases, the deficiencies associated with that means also increase. Therefore preferably the majority of the magnesium, and particularly preferably all of the magnesium carbonate is included in the preformed suspension.

The suspension of magnesium carbonate is preferably formed by dissolving a suitable water soluble magnesium compound, for example a magnesium sulphate, in water and adding to the resulting aqueous medium an aqueous alkaline solution of sodium carbonate, to precipitate it. Preferably the quantity of sodium carbonate, including any present in the reactants, is not more than that required in theory to precipitate the magnesium compound and any other constituent of the hydrous magnesium silicate present.

A silica precipitate may be formed by combining a suitable dissolved compound, for example syrupy sodium silicate solution containing by weight 29% SiO₂ and 8.8% Na₂O, with one or more sodium compounds. If the suspension of magnesium carbonate has been made by precipitation from a solution of a magnesium salt by an aqueous solution of one or more sodium compounds in the presence of a sufficient excess of sodium compound, the silica may be precipitated by adding a solution of the suitable silicon compound directly into the freshly precipitated carbonate. Alternatively, if an insufficient amount of sodium compound has been used to precipitate the magnesium carbonate and also the silica, further sodium compound may be added to the suspension of the magnesium compound and a solution of the suitable silicon compound then added. Alternatively, the silicon compound may be used as an aqueous solution containing insufficient sodium compound to precipitate it which may be added to the suspension containing the magnesium carbonate and sufficient sodium compound to cause precipitation of the silica. Any alternative method which results in precipitation of silica in the suspension of freshly precipitated magnesium carbonate may be used.

Preferably the lithium and fluoride components of the synthetic magnesium silicate are incorporated in the aqueous suspension of magnesium carbonate, e.g. by dissolving lithium and fluorine compounds in the suspension before precipitation of the silica. As an alternative to this suitable lithium and/or fluorine compounds may be introduced after precipitation of

the silica. Examples of suitable compounds are lithium carbonate, sodium silicofluoride, hydrofluoric acid, lithium fluoride, and lithium sulphate.

The resulting precipitate containing the components of the desired hydrous magnesium silicate must be maintained in the wet state until after the hydrothermal treatment. Preferably the entire aqueous suspension in which the precipitate is formed is subjected to hydrothermal treatment.

Hydrothermal treatment may be conducted by heating in the presence of a liquid phase for from 1 to 20 hours to crystallise the synthetic silicate. The degree of hydrothermal treatment required may vary considerably. At one end of the scale a mere boiling with agitation for, for example, up to about 6 hours may be conducted. Such a treatment tends to be suitable when the hydrous magnesium silicate has a relatively high fluorine content. At the other end of the scale it may be necessary to heat under pressure, for example at a temperature of at least 170°C and at a pressure of at least 100 psi, while still maintaining the presence of the liquid phase, to obtain suitable crystal growth. Such a hydrothermal treatment may suitably be applied to the production of hydrous magnesium silicates having a low fluorine content.

The aqueous suspension subjected to hydrothermal treatment contains excess dissolved sodium or lithium compound over that required to provide the cation of the hydrous magnesium silicate. The amount of the excess which is desirable for the formation of a hydrous magnesium silicate having good rheological properties will vary according to the particular magnesium silicate desired. It is not possible, therefore, to specify a lower limit of excess dissolved sodium or lithium compound but the amount of excess necessary for success may be optimised by simple experimental tests after the particular magnesium silicate has been selected. Preferably the excess of sodium or lithium compound is at least 25% and most preferably from 50% to 250%, for example from 50% to 200% on the basis defined above.

The crystalline material resulting from the hydrothermal treatment may be separated by filtration, is suitably washed, and is dried at a temperature not substantially exceeding 450°C.

The present invention may be operated to give a relatively high concentration of precipitate in the aqueous medium without serious viscosity problems arising, despite the use of a large excess of sodium or lithium ions during precipitation.

Preferably the process is operated to give a product concentration of at least 5%, for example from 5% to 10%, on a dried weight basis.

This represents a considerable increase in the productivity of the hydrothermal treatment apparatus in comparison with the previously used concentration of about 4% by weight.

At product concentrations of about 7% on a dried weight basis and above viscosity problems may be encountered in the manufacture of hydrous magnesium silicates containing appreciable quantities of lithium, for example about 1 atom of lithium per 8 atoms, of silicon. Preferably therefore, at high concentrations, relatively little, or no, lithium compounds are present during precipitation. Preferably at high concentrations the quantity of lithium is not more than 0.5 atoms, for example from 0.1 to 0.5 atoms, per 8 atoms of silicon during precipitation when the concentrations of reactants are such as to give a product concentration of at least 7% on a dried weight basis.

The present invention also makes possible the production of hydrous magnesium silicates having a crystal structure similar to that of natural hectorites and giving extremely fast dispersion in cold or hot aqueous media without sacrificing the excellent rheological properties characteristic of the processes of British Patents No. 1,054,111 and 1,213,122. As a general rule good dispersibility goes hand in hand with optical clarity in the resulting dispersion.

To ensure a product having good dispersibility the process should preferably be controlled carefully along the following lines.

The precipitation of the magnesium carbonate should preferably be conducted over an extended period of time for example over a period of from 30 minutes to 3 hours and preferably of from 1 to 2 hours. The precipitate of magnesium carbonate tends to be somewhat unstable with time. It is also liable to become less suitable for the practice of the invention if subjected to extreme conditions. Because of this the medium in which the water soluble magnesium compound is dissolved is preferably maintained at from room temperature to 60°C during the precipitation and the precipitate is preferably not boiled. The precipitation is preferably conducted by introducing the precipitant into an aqueous solution of the magnesium carbonate and not the reverse. The silica precipitate should be preferably formed gently, that is to say, gentle physical precipitation conditions should be used. Any precipitation conditions resulting in the formation of a large number of small seed crystals tend to reduce the quality of the product thus obtained. Generally, fast addition of a dissolved silicon compound to the suspension is to be avoided as is fast stirring during precipitation. In view of the variation in scale which may be used in carrying out the process of this invention and in view of the alternative procedures available to precipitate the silica it is not possible to define the term "gently" in absolute terms. For guidance however, the silica may suitably be precipitated over a period of at least 15 minutes preferably over a period of from 15 minutes to 1 hour.

Stirring rates may be determined by the scale but are desirably kept below about 1000 rpm preferably below about 200 rpm.

Boiling after precipitation but before pressure hydrothermal treatment, if used, may also assist in improving the optical properties of the product although it is not always necessary.

In the production of a particular hydrous magnesium silicate it may be possible to obtain a good product without maintaining all of the above process limitations at their optimum value and reference is made to Example 4 where a hydrous magnesium silicate product having good optical properties was obtained, even though the sodium silicate was added to the suspension quickly, using hand stirring at a speed of below 100 rpm.

The present invention also makes possible the production of hydrous magnesium silicates having a crystal structure similar to that of natural hectorite, having a high Bingham Yield Value, having excellent dispersion and optical properties, if the process has been suitably controlled and also having a low cation exchange capacity.

The products of British Patents No. 1,054,111 and 1,213,122 gave a high Bingham Yield Value but also had a cation exchange capacity of above 50 m.eq. per 100 grams. For certain applications a combination of good rheological properties and a low cation exchange capacity is advantageous. An example of such an application is found in the field of paint manufacture. In this case of course the optical properties of the clay are not important. According to a further feature the present invention therefore also provides synthetic hydrous magnesium silicates having a crystal structure similar to that of natural hectorite and having the general formula

$$[Si_8 (Mg_aLi_bH_c)O_{20}(OH)_{4-y}F_y]^{x-} \quad zM^+$$
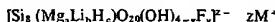
where a, b, y, z and M have the values hereinbefore ascribed to them, and having a Bingham Yield Value, as a 2% dispersion, in water having a hardness of 140 mg. per 1 calcium carbonate, of from 50 to 250 dynes per cm², and having a cation exchange capacity of from 25 to 50 m.eq. per 100 grams, and optionally, giving a cold dispersibility as hereinafter defined of less that 1.0.

The production of material having a cation exchange capacity within the above range is encouraged by controlling the quantity of sodium compound present when the magnesium carbonate is precipitated, to slightly below the stoichiometric quantity for the precipitation of the magnesium and any lithium or fluorine present and by controlling the hydrothermal treatment to a relatively short duration for example not more than 2 hours, and a relatively low temperature for example not more than 150°C preferably not more than 100°C.

In order that the invention may be understood more readily it is illustrated by means of the following examples.

Example 2 to 19, 21 and 23 to 29 are according to the invention.

Examples 1, 20 and 22 are inserted for comparative purposes only.

In the Examples the following tests are used.

Optical Density

The sample is added in 2% concentration by weight to distilled water, or aqueous solution as specified, at room temperature and the suspension brought to the boil and maintained boiling under reflux for 15 minutes with stirring. The suspension is cooled to room temperature and the optical density is measured using an EEL (Trade Mark) Absobrtiometer using a No. 603 filter and a 4 cm. cuvette.

Cold Dispersibility

The sample is added to distilled water to give a concentration of 2% by weight at a temperature in the range of 17°C-23°C and the suspension is stirred for 15 minutes using a 3000 rpm. stirrer. The optical density of the suspension is then measured immediately using the same apparatus as described above.

The range of optical densities of 0 to 0.60 so obtained is equivalent to a range of visual appearance from water clear to cloudy – translucent.

Static Gel Strength – Beam Balance

Gel strength is measured using a boiled dispersion of 2% by weight concentration (on a wet weight basis) containing 0.4 me/g Na_2 SO_4. A simple beam balance as used in laboratories to weigh samples is modified by attaching a rigid extension to one arm of the beam. An aluminium disc is suspended in the horizontal plane by a stiff vertical wire from the extension. A beaker is placed on the balance pan on the same side of the balance as the extension and the beam is then balanced by placing weights on the other pan. The beam is suspended. A standard diameter container containing the sample to be measured is raised upwardly towards the aluminium disc until the surface of the sample contacts the aluminium disc, and the vertical position of the container is then adjusted to zero the balance pointer the disc being held on the surface of the sample by surface tension.

Water is introduced slowly into the beaker until its weight has caused the aluminium disc to sink into the sample sufficiently to cause a standard deflection of the balance pointer and the static gel strength is the volume of the water introduced into the beaker.

For reference the apparatus used to obtain the beam balance results quoted in this specifi-

cation was so proportioned and the standard deflection was so selected, that water gave a Beam Balance reading of 12 and a gel which would just fail to flow from an upturned beaker would give a value of about 35.

EXAMPLES 1 & 2

The following separate solutions 1 to 4 were made up:—

Solution

1   183.5g $MgSO_4 7H_2O$, 10.1g $LiSO_4.H_2O$, 850g H_2O
2   250g Pyramid Nol sodium silicate (29% SiO_2, 8.8% Na_2O), 75.3g Na_2CO_3, 850g H_2O
3   75.3g Na_2CO_3, 600g H_2O
4   250g Pyramid Nol sodium silicate, 250g H_2O

"Pyramid" is a Trade Mark.

Solutions 3 and 4 together equal solution 2. In Example 1 solution 2 was added to solution 1 over 30 minutes thus precipitating Si and Mg values together according to the teaching of BP 1,213,122. In Example 2 solution 3 was added to solution 1 followed by solution 4 thus firstly precipitating the Mg values and secondly the Si values. The total time of addition of solutions 3 and 4 was 30 minutes and during this time the mixture of solutions was stirred at 100 rpm in each instance. The ingredients used correspond to a ratio of Si : Mg : Li : Na of 8 : 4.95 : 1.05 : 14.1 and the amount of water gave a magnesium silicate concentration, during hydrothermal treatment, of approximately 5% w/w in each Example. The resulting slurries were boiled for 1 hour at atmospheric pressure and each was divided into two samples. The two samples for each Example were treated hydrothermally at 250psig for 3 and 6 hours respectively at 207°C and the resulting hydrous magnesium silicate separated by filtration, washed and dried. The optical density of the product of each Example was measured.

Table I

OPTICAL DENSITY

Dispersion	Example 1		Example 2	
	Hours at 250psig			
	3	6	3	6
Dist. H_2O Na_2SO_4 Soln. 0.4 m.eq. Na^+/g	0.047 0.212	0.078 0.220	0.040 0.141	0.030 0.140

These results show that Example 2, which was according to the invention, gave a product of lower optical density than Example 1 which was not according to the invention using the same hydrothermal treatment. The optical density of the products of Example 2 decreased with increased duration of hydrothermal treatment whereas the opposite was true for Example 1. Each of the samples showed an X-ray diffraction pattern indicative of a crystal structure similar to that of natural hectorite and had good rheological properties.

EXAMPLES 3–9

The same procedure was used as in Example 2 the solutions used having compositions giving the overall atomic ratios

Si : Mg : Li : Na = 8 : 5.3 : 0.1 : 24

and a concentration of precipitate of 5% by weight.

The suspension, containing precipitated silica, at a 5% by weight concentration was hydro-thermally treated for 3 hours at 250psig at 207°C. A number of Examples were conducted in which the following conditions were varied.

(a)   Temperature of $MgSO_4 7H_2O$ solution (other solutions were at room temperature).
(b)   Rate of addition of the sodium carbonate and sodium silicate solutions.
(c)   Rate of stirring during addition of solutions 3 and 4.
(d)   Boiling after addition and before hydrothermal treatment.

The optical density of the product of each Example was measured as a 2% dispersion in distilled water after recovery, washing and drying. The process conditions varied and the optical density measurements obtained are summarised in Table II.

Table II

Example	MgSO₄7H₂O Temperature of °C	Total time of addition of carbonate and silicate sols.	Rate of Stirring	Boiling Time (mins)	Optical Density
3	20	By pouring in at max. rate	3000 rpm	0	not measured
4	20	„	hand stirred 100 rpm	0	0.05
5	20	Over 30 mins addition time	3000 rpm	0	0.10
6	20 ·	„	100 rpm	30	not measured
7	20	„	„	60	0.50
8	60	„	3000 rpm	0	not measured
9	60	„	100 rpm	30	0.03

Examples 3–7 show that a slow rate of addition of solutions 3 and 4, a slow rate of stirring, and boiling, all assist in the formation of a product having good optical properties. Where the optical density was not measured this was because the product had poor dispersion properties and, in fact, settled from the 2% dispersion formed for the purpose of optical density measurements. Examples 8 and 9 show that it is possible to obtain a product having really good optical properties using a warmed solution if the process features mentioned above are suitably controlled. All of the products had crystal structures similar to that of natural hectorite and good rheological properties.

EXAMPLES 10–14

The same procedure was used as in Example 9 with the sole modification, in Examples 11–14, that the quantity of water used in total was reduced to give the following weights of washed dried magnesium silicate per 100g slurry. The optical density, measured as a 2% dispersion in distilled water and the gel strength measured as a 2% dispersion in a solution of 0.8 me/g Na⁺ in distilled water is summarised in Table III together with the concentration used in each Example.

Table III

Example	g product/ 100g slurry	Optical Density	Gel strength Beam balance
10	5	0.06	93
11	6	0.09	45
12	7	0.015	55
13	8	0.005	78
14	9	0	62

In each of Examples 10–14 the hydrous magnesium silicate produced showed an X-ray diffraction pattern indicative of a crystal structure similar to natural hectorite.

A preparation was attempted using the overall atomic ratios of Example 10 and the co-precipitation method disclosed in British Patent No. 1,213,122. A stiff gel phase formed in the sodium silicate/sodium carbonate solution making it impracticable to continue the preparation.

EXAMPLES 15–18

The same procedure was used as in Example 9, but the quantities of chemicals were adjusted to give different atomic ratios and the times under hydrothermal pressure were also varied.

The cation exchange capacities were measured by standard laboratory methods. The preparations were used to make 2% dispersions by boiling for 15 minutes in tapwater of hardness 140mg CaCO₃/litre and the Bingham Yield Values (BYV) were measured on a Fann Viscometer. The optical densities of the same dispersions, i.e. 2% in tap water having a hardness of 140mg CaCO₃/litre, are also given. The process and results are summarised in the following table.

Table IV

Example	Overall atomic ratio			Hours at 250 psi	Cation exch. capacity (m.eq./100g.)	B.Y.V. (dyne/cm²)	Optical Density
	Si	Mg	Li				
15	8	5.3	0.7	3	44	191	0.10
16	8	5.3	0.5	3	31	162	0.11
17	8	5.3	0.5	6	49	143	0.11
18	8	5.3	0	3	34	120	0.20

It is seen that these preparations combine low cation exchange capacity with high BYV and low optical density. In fact the optical density obtained in these Examples compares well with that obtained in Example 9 the apparent difference being attributable to the difference in the water used to make up the dispersion.

EXAMPLES 19–22

The same procedure was used as in Example 2 with the modifications that in Examples 20 and 22 which are not according to the invention Na_2CO_3 was replaced by an equivalent amount of NaOH and in Examples 21 and 22 the amount of Na_2CO_3 and NaOH was slightly greater being equal to the amount required in theory to precipitate the magnesium and lithium values in solution 1.

The gel strength of the products was measured by the Beam Balance method described above.

Table V

Example No.	Solution 3 compound	% equiv. to Mg & Li in Solution 1	Gel strength Beam Balance	Cold dis- persibility	Optical Density
19	Na_2CO_3	94	46	0.245	0.08
20	NaOH	94	45	∞	∞
21	Na_2CO_3	100	48	0.60	0.06
22	NaOH	100	50	∞	0.69

In Examples 19 and 20 a total of 14.1 and in Examples 21 and 22 a total of 15.6 atoms of Na were present per 8 atoms of Si.

EXAMPLES 23–27

In a consecutive series of experiments to the procedure used was that of Example 2 with the following modifications.

The solutions used contained an amount of Na_2CO_3 equivalent to 14.7 atoms of Na for every 8 atoms of Si.

The lithium content of solution 1 was reduced to half and was compensated for by an increase in the quantity of magnesium and the concentration of the solutions was adjusted to give a product concentration of 6% by weight after hydrothermal treatment. Solution 3 was added over 60 minutes and solution 4 over 15 minutes.

The products were isolated and examined and the results are summarised in Table VI.

Table VI

Example No.	Cold Dispersibility	Optical Density	Gel strength Beam Balance
23	0.26	0.15	52
24	0.29	0.11	50
25	0.28	0.13	48
26	0.30	0.16	42
27	0.33	0.18	54

By way of comparison the cold dispersibility of the product of consecutive series of pre- parations conducted using the procedure of Example 1 but on a larger scale and using a

concentration of product after hydrothermal treatment of 4.1 % varied as follows
∞, ∞, ∞, 0.82, 0.29, ∞, 0.95, 0.57, 0.57, 0.35.

EXAMPLES 28–29
5   The following solutions were made up:—
     1.   1603.5 Kg $MgSO_4 7H_2O$, 37.1 Kg $Li_2SO_4 H_2O$, 4540 Kg H_2O
     2.   671 Kg Na_2CO_3, 3589 Kg H_2O
     3.   1910 Kg Pyramid No. 1 sodium silicate 2553 Kg H_2O
     "Pyramid" is a Trade Mark.
10   Solution 2 was added to solution 1 stirred at 100 rpm over a period of 2 hours, the tem-
perature of the mixed solutions being maintained at 40°C approximately.
     Solution 3 at a temperature of 20°C was added to the suspension resulting from mixing
solutions 1 and 2 starting immediately after that mixing had been completed. The resulting
suspension was boiled to expel CO_2 and was then autoclaved after heating up over a period
15   of 2 hours for 6 hours at a pressure of 250 psig. The resulting product was washed and dried
at a temperature of 150°C. The weight of dried precipitate corresponded to a 6 % by weight
concentration in the autoclave. The resulting material had a crystal structure similar to that
of a natural hectorite. Its rheological properties were tested by the "Beam Balance" method
and its Bingham Yield Value was also determined.
20   The Example was also repeated using a smaller quantity of water so as to give a 9 % con-
centration by weight in the autoclave and the product tested in the same manner.
     The results are summarised as follows:—

Table VII

Example	Concentration	Bingham Yield Value	Gel Strength Beam Balance
28	7 %	135	49
29	9 %	163	43

WHAT WE CLAIM IS:—
     1.   A process for the synthesis of a hydrous magnesium silicate having a crystal structure
similar to that of hectorite and having the general formula
35                          $[Si_8 (Mg_a Li_b H_c)O_{20}(OH)_{4-y}F_y]^{2-}$ zM^+
wherein a, b, c, y, z and M have the values:—
                              a is from 4.95 to 5.7
                              b is from 0 to 1.05
                              c is from 0 to <2
40                            $a+b+c$ is from >4 to <8
                              y is from 0 to <4
                              $z = 12-2a-b-c$
                              M is Na^+ or Li^+
comprising the sequential steps of forming an aqueous suspension of magnesium carbonate,
45   forming a silica precipitate in the aqueous suspension of magnesium carbonate, the propor-
tions of magnesium provided by the magnesium carbonate and of silica precipitated in the
suspension of magnesium carbonate corresponding to that of the formula of the magnesium
silicate, maintaining the resulting mixture of magnesium carbonate and silica in the wet
state and subjecting it to hydrothermal treatment by heating it in an aqueous medium and in
50   the presence of the remaining constituents of the magnesium silicate in proportions within
the ranges specified in the general formula thereof and in the presence of excess dissolved
sodium or lithium compound over that required to form the cation thereof until crystal
growth occurs and separating the resulting crystalline product.
     2.   A process as claimed in claim 1 wherein the aqueous suspension of magnesium car-
55   bonate is formed by dissolving a water soluble magnesium compound in an aqueous medium
and adding to the aqueous medium an aqueous solution of sodium carbonate so as to pre-
cipitate the magnesium carbonate.
     3.   A process as claimed in claim 2 wherein the aqueous solution of sodium carbonate is
added to the aqueous medium in which the water soluble magnesium compound is dissolved
60   over a period of from 30 minutes to 3 hours.
     4.   A process as claimed in claim 2 or 3 wherein the aqueous medium in which the water
soluble magnesium compound is dissolved is maintained at a temperature of from room
temperature to 60°C during the precipitation.
     5.   A process as claimed in any one of claims 2 to 4 wherein the quantity of sodium car-
65   bonate is not more than that required in theory to precipitate the magnesium carbonate

and any other constituent of the hydrous magnesium silicate present.

6. A process as claimed in any preceding claim wherein the silica is precipitated over a period of from 15 minutes to 1 hour.

7. A process as claimed in any preceding claim wherein the excess of sodium or lithium compound during hydrothermal treatment is from 50% to 200% over that required to form the cation of the hydrous magnesium silicate.

8. A process as claimed in any preceding claim wherein the concentrations of the reactants used is such as to give a product concentration on a dried weight basis of at least 5%.

9. A process as claimed in claim 8 wherein the concentrations of reactants are such as to give a product concentration on a dried weight basis of at least 7% and the quantity of lithium present during precipitation is not more than 0.5 atoms for every 8 atoms of silicon present.

10. A synthetic hydrous magnesium silicate having a crystal structure similar to that of natural hectorite and having the general formula

$$[Si_8 (Mg_aLi_bH_c)O_{20}(OH)_{4-y}F_y]^{z-} \quad zM^+$$

where a, b, c, y, z and M have the values hereinbefore ascribed to them, and having a Bingham Yield Value, as a 2% dispersion, in water having a hardness of 140 mg. per 1 calcium carbonate, of from 50 to 250 dynes per cm², and having a cation exchange capacity of from 25 to 50 m.eq. per 100 grams.

11. A synthetic hydrous magnesium silicate as claimed in claim 10 having a cold dispersibility as herein defined of less than 1.0.

12. A process substantially as herein described with reference to any one of Examples 2 to 19, 21 and 23 to 29.

13. A hydrous magnesium silicate which has been produced by a process as claimed in any one of claims 1 to 9 and 12.

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